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(54) **Title:** PURIFICATION OF GAS MIXTURES

(57) **Abstract:** Gas purification and selective removal of specific gasses from gas mixtures is of importance for many processes. The method and apparatus of this invention can remove selectively specific gasses like carbon monoxide from gas mixtures that contain hydrogen. The hydrogen and CO containing gas mixture is brought in contact with one side of a membrane, while on the other side of the membrane an oxygen containing gas is provided. The CO will bind to the membrane or to certain chemical species in this membrane on one side, move to the other side of the membrane, where the CO is converted with oxygen to CO2.

PURIFICATION OF GASMIXTURES

The invention has as its purpose to provide a method and apparatus for selectively removing gasses from gas mixtures by using a membrane. The method and apparatus according to the invention are specifically suitable for the selective removal of Carbon Monoxide from mixtures containing; hydrogen, water vapor and Carbon dioxide.

A fuel processor is an apparatus that converts fossil fuels like natural gas (LG), LPG, methanol, petrol and diesel into a gas mixture containing hydrogen. This gas mixture, called reformate, produced by the fuel processor, can be used to feed a fuel cell, like a PEM-fuel cell. The PEM-fuel cell is an efficient electro chemical device that can convert hydrogen or hydrogen containing gas mixtures into electrical power and heat. Fuel processors, PEM fuel cells and PEM fuel cell stacks are generally known. Known fuel processors deliver a gas mixture that contains traces of carbon monoxide up to a level of several percent. Carbon monoxide is known to degrade the performance of PEM fuel cell, even at very low concentrations. It is therefore advantages to remove the CO from the gas mixture down to a level of 50 PPM, preferably 20 PPM (0,002%) or less before it is fed to the anode of the fuel cell. Several methods for removing CO from reformate have been proposed. Some of these methods remove the CO before the fuel cell, while others remove the CO in the fuel cell.

A known method is the addition of air to the reformate prior to feeding the reformate to the anode gas stream of the PEM fuel cell. The oxygen oxidizes the CO to CO2 at the anode of the fuel cell. This method yields acceptable results, but has severe drawbacks. The oxidation of CO is not selective, and some of the oxygen reacts with hydrogen, thus reducing efficiency and can damage the fuel cell. Another drawback of this method is that it requires accurate measurement of the CO concentration and accurate metering of the air.

Some disadvantages of the above-described method are eliminated by the CO-removal method of NL1998001010140. In this patent application a material and method for selective removal of CO from reformate is claimed. According to NL1998001010140 a precious metal catalyst is applied on a porous carrier in a reactor, a small amount of oxygen or air is metered into the reformate stream at the inlet of this reactor, and this catalyst is oxidizing the CO to CO2. The method still has the drawback of oxidizing part of the hydrogen, and the necessity to accurate

measurement of the CO concentration and accurate metering of the air or oxygen flow.

The method and apparatus according to the invention provides selective removal of a gas from a gas mixture. The method and apparatus are especially effective for removal of CO from a hydrogen, CO2 and water vapor containing gas stream. According to the invention, a membrane and means to fit this membrane in are provided, with on one side the CO-containing gas, and on the other side, a oxygen containing liquid or oxygen containing gas like air. The membrane according to the invention is able to selectively absorb the CO, by means of a chemical reaction or physical adsorption on the first side to form a CO containing compound (CO-X), transport this CO containing compound to the other side of the membrane, and react the CO-containing compound with oxygen to form CO2 on the second side.

Reaction on the first side $CO + X \rightarrow CO\text{-}X$

Reaction on the second side $CO\text{-}X + O2 \rightarrow CO2 + X$

The membrane according to the invention preferably consists of a porous polymer containing a liquid that is able to transport the CO containing compound (X). This liquid could be water or a solution of selected salts, these salts being preferably catalytic active. An example of a catalytically active salt solution is a mixture of Palladium chloride, Ruthenium chloride, Copper (II) Chloride, Lithium Chloride. Besides water and salts, the solution can contain several additives than improve performance or stability. Examples of these additives are; silica, aluminia, zeolites and (conductive) carbon black, pH controllers and thickeners. The membrane has preferably a high porosity and a small pore size, sufficiently small for immobilizing the liquid. The shape of the membrane can be flat, or tube like, as for example a hollow fiber. The flows on both sides of the membrane can be parallel, counter flow or cross-flow.

According to the invention the membrane can be coated on one side, or on both sides with a material that promotes the removal of CO from the reformate, or promotes the conversion of the CO containing compound to CO2 and the original compound as it was prior to the formation of the CO containing compound.

According to the invention it is possible to eliminate porosity locally by densification at increased temperature and pressure, This densification is done prior to impregnation of the membrane, and avoids use of expensive material in non active area's like edges and seals.

For the removal of large quantities of gas, the membrane surface area can be increased, and the amount of gas that can be removed will typically be linear with the surface area. If flat membranes are used the capacity can be increased by increasing

the size of the membrane, or by using more membranes in parallel or in series connection. Combinations of parallel and series connected membranes is also possible. To increase the membrane surface areas wile keeping the module volume low, the membrane can be spirally wound or hollow fiber membranes can be used.

The porous membrane can consist of a porous polymer film, a non-woven material like paper, or a textile web like a fabric or cloth. Suitable polymers for the porous film are for example PTFE, PVDF, PE or PES. Suitable fibrous materials are several organic fibers like PE, and inorganic fibers glass and graphite.

The method and apparatus according to the invention can be integrated in to other components of the fuel cell system. Integration is for example possible in the fuel cell stack, in the fuel processor, or in the moistening units. If the CO removing membrane is integrated in the fuel cell stack, the reformate gas stream flows along the CO removing membrane prior to the anodes of the fuel cells, while the cathode outlet gas stream of the fuel cells can be used for the CO oxidation on the other side of the membrane. The oxygen content at the cathode outlet is sufficient for oxidation of the small amounts of CO. An advantage of this integration is the compactness of the system, and easy control of gas temperatures and water content.

According to one other embodiment of the invention it is possible to integrate, the CO-removing membrane or membranes into the fuel processor were it is positioned at the outlet. Advantages of this integration are compactness of the system, improved thermal efficiency, and easy control of gas temperatures and water content.

Integration of the CO-removing membrane is also possible in the moistening units. Moistening is an important part of a fuel cell system. The wet membrane that removes the CO from the gas stream can add water to this same gas stream. In such a integrated system provisions are required to avoid drying of the membrane.

A potential risk of the membrane according to the invention is loss of liquid. This can be avoided or reduced by making the surface or both surfaces of the membrane hydrophobic. The Hydrophobic behavior can be obtained by treating the surface with special chemicals, or for example by laminating a hydrophobic gas permeable film to one or both sides of the membrane.

An other potential risk of the CO removal system according to the invention is transport of metal ions from the CO removing membrane to the fuel cell trough a water film on the inside of the connections. This is avoided by using a hydrophobic connection between both units. Such a hydrophobic connection is for example a hydrophobic tube or hydrophobic ring on the inside of a connecting tube.

Example

A film of porous UHMWPE, was made non porous at the edges by pressing this area at a temperature of 100 degrees Celsius. The remaining porous part (400 x 400mm) of the film was impregnated with a solution containing; 0,02 M $PdCl_2$, 1 M $CuCl_2$ and 1 M $Cu(NO_3)_2$. The film was framed, and placed between two airtight chambers, thus realizing gas separation between these chambers. The chambers and membrane were placed in an oven at a temperature of 70 degrees Celcius.

One chamber was filled with a mixture of 45% hydrogen, 33% nitrogen, 20 % CO_2 and 2% CO. The other chamber was filled with air that was saturated at 70 degrees Celsius with water vapor. The CO concentration was measured in both chambers. After 10 minutes the CO concentration had dropped below the CO detection limit of the sensor (<<1PPM). In the other chamber, no CO was detected.

CONCLUSIONS

1. A method and apparatus for the selective removal of a gas or gasses from a gas mixture, characterized that a porous membrane is used, and this membrane is in contact on one side with the gas mixture containing the gas or gasses to be removed, and on the other side in contact with a gas, a liquid or a combination of gas and liquid that can react with the gas to be removed or a compound containing the gas to be removed.
2. A method and apparatus according to claim 1, characterized in that the membrane is porous and the pores are filled with a liquid.
3. A method and apparatus according to any one of the proceeding claims, characterized in that the membrane is filled with a solution of salts.
4. A method and apparatus according to claim 3, characterized in that salt solution comprises a Pd (II) salt, a Cu (II) salt and a Cu (II) halide.
5. A method and apparatus according to any of the preceding claims containing a membrane characterized in that this porous membrane is made of polymer.
6. A method and apparatus according to claim 5, containing a polymer membrane characterized in that the porous polymer is PES, UHMW-PE, PVDF or PTFE.
7. A method and apparatus according to any of the preceding claims, containing a membrane characterized in that the membrane contains a solid that can absorb and immobilize a liquid.
8. A method and apparatus according to claim 7, containing a membrane, and this membrane contains a fluid immobilizing solid, characterized this solid is contains silica.
9. A method and apparatus according to any of the preceding claims containing a membrane characterized in that the membrane is conductive to electrons.
10. A method and apparatus according to any of the preceding claims containing a membrane characterized in that the membrane is conductive to ions.
11. A method and apparatus according to any of the preceding claims containing a membrane characterized in that the membrane has electrical conductive layers on both sides that can operate as electrodes.
12. A method and apparatus according to any of the preceding claims containing a membrane characterized in that the membrane is coated one side or both side with a catalyst.

13. A method and apparatus according to any of the preceding claims characterized in that the apparatus is connected to an apparatus that converts hydrocarbons to hydrogen containing gas mixtures.
14. A method and apparatus according to any of the preceding claims characterized in that the apparatus is connected to a fuel cell.
15. An apparatus according to claim 14 that is connected to a fuel cell having an hydrogen containing gas inlet, and a oxygen containing gas inlet and a membrane separating these two gas mixtures, characterized in that the hydrogen containing gas stream that leaves the apparatus of the invention is connected to the anode inlet of the fuel cell, and the oxygen containing outlet of the fuel cell is connected to the apparatus oxygen containing gas inlet.
16. A method and apparatus according to any of the preceding claims characterized in that the apparatus is integrated in the fuel cell stack.
17. A method and apparatus according to any of the preceding claims characterized in that the apparatus is integrated in the fuel processor.
18. A method and apparatus according to any of the preceding claims characterized in that the apparatus is integrated in the moistening unit.
19. A method and apparatus according to any of the preceding claims characterized in that the gas to be removed is carbon monoxide.
20. A method and apparatus according to any of the preceding claims characterized in that the gas channels between the apparatus and the fuel cell are completely or partly hydrophobic

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/22 B01D61/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 147 754 A (WARD III WILLIAM J) 3 April 1979 (1979-04-03) column 2, line 58 -column 4, line 9; claim 1; figure 1 ---	1-3,5,7
X	EP 0 349 204 A (BEND RES INC) 3 January 1990 (1990-01-03) page 2, line 48 -page 3, line 7 page 7, line 40 -page 7, line 41 page 7, line 52 -page 8, line 9; figure 1 ---	1,2,5,7
X	EP 0 434 562 A (MEDAL 1 P) 26 June 1991 (1991-06-26) abstract; figure 1 ---	1
A	EP 0 989 093 A (AIR PROD & CHEM) 29 March 2000 (2000-03-29) claim 1; figure 1 ---	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Semino, D

INTERNATIONAL SEARCH REPORT

national Application No
PCT/NL 01/00389

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 474 858 A (MAKINO HIROSHI ET AL) 2 October 1984 (1984-10-02) abstract ---	2-8
A	EP 0 435 724 A (PETROLEUM ENERGY CENTER FOUND ;SHOWA SHELL SEKIYU (JP)) 3 July 1991 (1991-07-03) abstract; figure 2 -----	13-18

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 4147754	A	03-04-1979	NONE			
EP 0349204	A	03-01-1990	JP	2131586	A	21-05-1990
EP 0434562	A	26-06-1991	FR	2655873	A	21-06-1991
			CA	2032560	A	21-06-1991
			DE	69021851	D	28-09-1995
			DE	69021851	T	11-01-1996
			ES	2077049	T	16-11-1995
			JP	4012001	A	16-01-1992
EP 0989093	A	29-03-2000	US	6114400	A	05-09-2000
			AU	736483	B	26-07-2001
			AU	4760099	A	06-04-2000
			NO	994552	A	22-03-2000
US 4474858	A	02-10-1984	JP	58011003	A	21-01-1983
			JP	61053103	B	15-11-1986
			DE	3225837	A	03-02-1983
			GB	2104905	A,B	16-03-1983
EP 0435724	A	03-07-1991	JP	3201370	A	03-09-1991
			DE	69017871	D	20-04-1995
			DE	69017871	T	06-07-1995
			US	5149600	A	22-09-1992